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Veenstra, S. C.; Stalmach, U.; Krasnikov, V. V.; Hadziioannou, G.; Jonkman, H. T.; Heeres, A.; Sawatzky, G. A.

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Energy level alignment at the conjugated phenylenevinylene oligomer/metal interface

S. C. Veenstra, U. Stalmach, V. V. Krasnikov, and G. Hadziioannou[a)]
Department of Polymer Chemistry, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

H. T. Jonkman, A. Heeres, and G. A. Sawatzky
Laboratory of Solid State and Applied Physics, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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In this letter we report an investigation of the interfacial electronic structure formed by metals and conjugated oligomers using ultraviolet photoelectron spectroscopy. Au and Ag were used as metal substrates for two five-ring phenylenevinylene oligomers: unsubstituted *p*-bis[(*p*-styryl)styryl]benzene (P5V4) and the analogous oligomer with 2-methoxy-5-(2'-ethyl-hexyloxy) substitution on the central ring (MEH-P5V4). We found for all interfaces a lowering of the energy levels of the organic overlayer by 0.4–1.2 eV. Remarkably, this energy lowering, presumably due to interface dipole layers, was always such as to keep the hole injection barrier nearly constant and therefore at most weakly sensitive to the work function of the metal or the ionization potential of the oligomer. © *2000 American Institute of Physics.* [S0003-6951(00)01216-X]

The charge transfer process at the interface between an electrode and a polymeric semiconductor plays a key role in the performance of optoelectric devices like polymer light-emitting diodes (*p*LEDs) and photovoltaic devices (PVDs). These devices typically consist of one or more polymer layers sandwiched between two electrodes. The transfer process at the interface between the contact and the active layer is a function of the barrier height between the Fermi energy level of the electrode and the frontier orbital levels of the polymer layer. In order to estimate the injection barrier one usually assumes a rigid band model and an alignment of the vacuum levels at the interface. However, these assumptions ignore the possible formation of dipole layers or covalent bonds at the interface and doping of the interfacial region. Although measurements of the vacuum level alignment are important for understanding device behavior and optimizing device efficiency, they have seldom been reported for the interface between metals and phenylenevinylene oligomers.[1–3]

Here we report ultraviolet photoelectron spectroscopy (UPS) measurements on the interfaces between metals (Au and Ag) and two different five-ring phenylenevinylene oligomers (P5V4's), unsubstituted (P5V4) and 2-methoxy-5-(2'-ethyl-hexyloxy)-substituted P5V4 (MEH-P5V4) (see inset Figs. 1 and 2, respectively). These oligomers can be used for optoelectronic applications and as model systems for the two most widely used corresponding conjugated polymers. The advantage of using these oligomers instead of the polymers is that their high chemical purity and relatively low mass enables us to prepare thin films *in situ* by deposition of the oligomer on a cleaned metal surface under ultrahigh vacuum (UHV) conditions.

In all cases we measured a misalignment between the vacuum levels of the metal and the oligomer. The levels of the oligomers shift downward relative to the energy levels of the metal (a negative shift). The magnitude of this shift is between 0.4 and 1.2 eV, depending on the metal as well as on the oligomer. The observed energy level alignment may have a strong effect on the charge injection process at the metal/oligomer interface as it is found in LEDs and PVDs.

All experiments were performed in a single UHV chamber with a base pressure of 10^{-9} mbar equipped with a He discharge lamp (He I, $h\nu = 21.22$ eV) and an effusion cell of our own design. A hemispherical analyzer, in combination with a lens system, was used as electron energy analyzer with an overall resolution of 150 meV. The metal substrates were cleaned by polishing and washing in an ultrasonic bath with toluene and acetone as solvents. Next, the substrates were placed in a sampleholder on a x,y,z stage. Under UHV conditions, the substrates were Ar^+-ion sputtered in order to obtain UPS spectra without features from impurities or adsorbed overlayers. During measurements, a bias voltage of -4.00 V was applied to the sampleholder to clear the low-kinetic-energy cutoff of the spectrum. The oligomers were synthesized and purified as described elsewhere.[4,5] The oligomer/metal interfaces were formed by slow molecular beam deposition monitored by a calibrated thickness monitor, after degassing the effusion cell for several hours at 120 °C. Typical sublimation temperatures range from 225 to 275 °C and the pressure ranges from 0.5×10^{-7} to 2×10^{-7} mbar, giving a deposition rate of several monolayers per minute. The oligomer film thickness used in determining the energy level offset was typically 5–10 nm.

Figure 1 illustrates how an interfacial energy diagram, including the presence of an electric field, is deduced from two UPS spectra. The figure shows the He I UPS spectra of Au (left) and P5V4 on Au (right). Both spectra were recorded while a bias voltage of -4.00 V between sample and analyzer was applied. The energy diagram of the interface is shown in the middle of Fig. 1. The y axis represents the kinetic energy of the photoelectrons at the entrance slit of the

a)Electronic mail: hadzii@chem.rug.nl

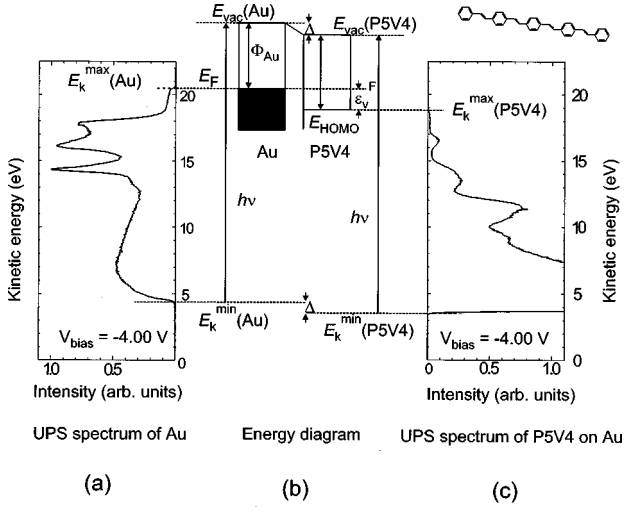

FIG. 1. Method for determining the energy diagram of the metal/oligomer interface using the ultraviolet photoelectron spectra of the metal and the oligomer. The spectra were recorded with a bias of -4.0 V between sample and analyzer. The y axis represents the kinetic energy of the photoelectrons at the entrance slit of the analyzer. (a) Photoemission of the Au substrate. (c) photoemission of 5–10 nm of P5V4 on the Au substrate. (b) Energy diagram of the Au/P5V4 interface. E_k^{max}(Au): maximum kinetic energy of a photoelectron excited from Au with $h\nu$: photon energy (21.22 eV); E_k^{max}(P5V4): maximum kinetic energy of a photoelectron excited from P5V4; E_k^{min}(Au): minimum kinetic energy of a scattered photoelectron excited from Au; E_{vac}(Au): vacuum level of Au; E_k^{min}(P5V4): minimum kinetic energy of a scattered photoelectron from P5V4; E_{vac}(P5V4): vacuum level of P5V4; Φ_{Au}: work function of Au; E_{HOMO}: energy level of highest occupied molecular orbital of P5V4, ϵ_v^F: hole injection barrier or the energy difference between the Fermi level of Au and the HOMO level; Δ: vacuum level shift. The structure of P5V4 is shown at the top, right.

analyzer. The total spectrum consists of photoelectrons suffering no energy loss processes on their way out of the solid providing information on the binding energies of the occupied states of the solid, and scattered electrons which have suffered energy loss which contributes to a structured background. The high-kinetic-energy onset of the spectra corresponds to emission of electrons from the Fermi level of the metal $[E_k^{max}(\mathrm{Au})]$ or from the highest occupied molecular orbital (HOMO) of the oligomer $[E_k^{max}(\mathrm{P5V4})]$. The low-kinetic-energy cutoff $[E_k^{min}(\mathrm{Au}), E_k^{min}(\mathrm{P5V4})]$ corresponds to electrons having suffered energy loss processes and ended up at the minimum kinetic energy in the solid required to escape into the vacuum.

Thus the position of the vacuum level of a material in the diagram is determined by adding 21.2 eV to the cutoff energy to give E_{vac}(Au) and E_{vac}(P5V4). Now one can determine the work function of Au using:

$$\Phi_{Au} = h\nu - [E_k^{max}(\mathrm{Au}) - E_k^{min}(\mathrm{Au})] \quad (1)$$

and the position of the HOMO level of P5V4 according to:

$$I_s = h\nu - [E_k^{max}(\mathrm{P5V4}) - E_k^{min}(\mathrm{P5V4})]. \quad (2)$$

By comparison of the two UPS spectra, we can construct an energy diagram as shown in the middle of the plot and determine the positions of the energy levels at both sides of the interface. We can determine the difference (Δ) between the vacuum levels of the metal and the oligomer layer using:

$$\Delta = E_k^{min}(\mathrm{P5V4}) - E_k^{min}(\mathrm{Au}). \quad (3)$$

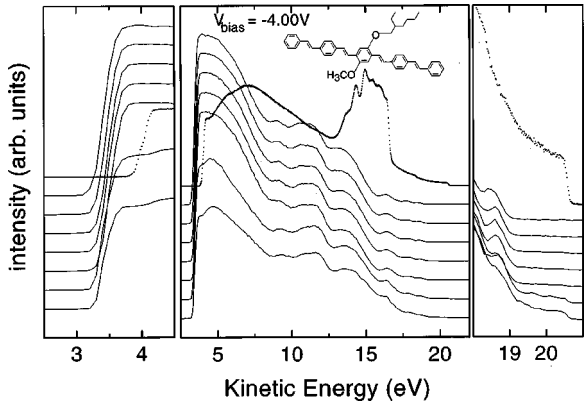

FIG. 2. UPS spectrum of MEH-P5V4 on Ag as function of the deposition time (thickness). All spectra were recorded with a bias of -4.0 V between sample and analyzer. The x axis represents the kinetic energy of the photoelectrons at the entrance slit of the analyzer. The dotted line is the spectrum from the polycrystalline Ag substrate. The plots on the right- and left-hand side show an enlargement of the central plot. After each spectrum, the thickness of the MEH-P5V4 layer was increased by approximately 0.5–1 nm, except for the last two spectra where the thickness was increased by several nanometers. The inset in the middle plot shows the structure of MEH-P5V4.

Since the vacuum level of the oligomer is lower than the vacuum level of Au, the electric field points from the oligomer $(\delta+)$ to the metal $(\delta-)$, making $\Delta<0$ (as defined in Ref. 3). In this case, the vacuum level shift leads to an increase of the barrier for hole injection $(\epsilon_v'^F)$ according to:

$$\epsilon_v'^F = I_s - \Phi_{Au} - \Delta. \quad (4)$$

This hinders hole injection from Au to P5V4, but facilitates electron injection from the fermi level of Au to the lowest unoccupied molecular orbital (LUMO).

In Fig. 2 we show the interface formation of MEH-P5V4 on a clean Ag substrate. In the center, the full spectra are given. The bottom spectrum shows the UP spectrum of the Ag substrate with a thin layer of MEH-P5V4 evaporated on top (in the order of 1 nm). The subsequent spectra show the photoemission of the surface with increasing MEH-P5V4 thickness (0.5–1 nm increase per deposition step). The top line, with the largest offset, shows the Ag spectrum with the Fermi edge well resolved (at $h\nu - \Phi_{Ag} + V_{bias} = 20.6$ eV). At the right-hand side, the gradual change in the HOMO region is depicted in more detail. As the film grows thicker, the features arising from the Fermi level of Ag give way to the pure MEH-P5V4 spectrum. The low-kinetic-energy cutoff region is plotted at the left-hand side of Fig. 2. The shift in the onset (Δ) is complete after depositing approximately 1 nm on the substrate, it does not increase further with film thickness. This result indicates that one or very few molecular layers are involved in the process.

The upper two spectra of MEH-P5V4 show a small shift of 0.1 eV towards lower kinetic energy. A slight charging of the sample may cause this shift, which is within our measurement accuracy. The lowering of the vacuum level is caused by an electric field at the interface due to (partial) charge transfer in the interfacial region. The exact mechanism creating the electric field is so far unknown. Several processes can cause an electric field at an interface, for example, electron transfer from a donor to an acceptor, image effects, tailing of the electron cloud of the metal towards the

TABLE I. UPS measurements on P5V4 and MEH-P5V4 ($\Phi_{Au}=5.1\pm0.1$ eV and $\Phi_{Ag}=4.4\pm0.1$ eV). Δ represents the vacuum level shift; I_s, ionization energy; ϵ_v^F, measured hole injection barrier; $\epsilon_v'^F$, calculated hole injection barrier using Eq. (4).

Interface	Δ (eV)	I_s (eV)	ϵ_v^F (eV)	$\epsilon_v'^F$ (eV)
P5V4 / Au	-1.0 ± 0.1	5.6 ± 0.1	1.4 ± 0.1	1.5 ± 0.3
P5V4 / Ag	-0.4 ± 0.1	5.6 ± 0.1	1.7 ± 0.1	1.6 ± 0.3
MEH-P5V4 / Au	-1.2 ± 0.1	5.2 ± 0.1	1.2 ± 0.1	1.3 ± 0.3
MEH-P5V4 / Ag	-0.5 ± 0.1	5.3 ± 0.2	1.3 ± 0.2	1.4 ± 0.4

adsorbent causing dipoles or metal induced gap states, or chemical interactions between metal and overlayer.[6–8]

Charge transfer at the interface formed by similar PPV oligomers on a Ca substrate was observed by Park *et al.*[1,2] The charge transfer caused an overall energy level bending of 0.5 eV in a space-charge region extending over 10 nm. The energy level bending in their experiment indicates electron transfer from the metal to the organic overlayer making $\Delta>0$, which is opposite to the values reported here.

Image potential effects lower the ionization energy of insulators and semiconductors adsorbed on metal surfaces. This stabilizing effect is linearly proportional to $1/d$ where d is the distance between the metal surface and the photoionized molecule.[9,10] Such a distance dependence is not reflected in a dependence on the film thickness in this study (see Fig. 2), indicating that the image potential effect is either small for even the thinnest layer measured or compensated for by another electro-static effect. Chemical interactions at the interface formed by evaporating Al on a sexithiophene layer have been reported[3] with a significant charge transfer from the metal to the oligomer, resulting in the formation of a bond between the oligomer and the metal. Such a charge transfer causes an electric field pointing from the metal towards the organic layer ($\Delta>0$). For most metal–organic interfaces the dipole is negative (see for example Fig. 15 in Ref. 6), similar to our measurements.

Table I summarizes the results of the UPS measurements. The shift between vacuum levels at the interface is negative in all cases, moving the energy levels of the oligomer downward relative to the levels of the metal. The magnitude of the shift is larger for Au than for Ag and also depends on the oligomer: the substituted oligomer causes a larger shift. The ionization energy seems to be independent of the metal substrate and compares well with previously reported values for similar P5V4s.[11] The hole injection barrier can be obtained in two ways: by measuring the energy difference between the high kinetic energy onset of the metal and the oligomer, as shown in Fig. 1 (ϵ_v^F), or by using Eq. (4) ($\epsilon_v'^F$). The differences between the values for the same injection barrier (see column 4 and 5 in the table) give an indication of the systematic error. The values clearly show that the misalignment of the vacuum levels strongly influences the hole injection barrier and acts as to keep the barrier almost independent of the work function of the metal substrate.

In conclusion, we reported UPS measurements of the interface formed by evaporating PPV-like oligomers onto metals (Ag and Au). We found for all these interfaces a misalignment between the vacuum levels of the metal and the organic overlayer. This shift of levels, presumably caused by an interfacial dipole layer, strongly influences the hole injection barrier in such a way as to keep this barrier nearly constant and therefore at most weakly sensitive to the work function of the metal or the ionization potential of the oligomer. Knowledge of this interfacial dipole layer is therefore crucial for understanding the electrical characteristics of oligomer-based electronic devices.

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